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Process for recovering metal values

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(71) Applicant(s)
Pasminco Australia Limited

(72) Inventor(s)
Eric Roche; Paul Freeman

(74) Agent/Attorney
Griffith Hack,GPO Box 1285K,MELBOURNE VIC 3001

(56) Related Art
US 4676828

The specification describes a counter-current two stage process for recovering metal values from a metal sulphide. The process involves leaching a metal sulphide ore or concentrate in sulphuric acid in the presence of ferric ions at atmospheric pressure and elevated temperature whilst sparging with oxygen. Fresh sulphuric acid is added to the second stage whilst the ore or concentrate is added to the first stage. Leachate from the second stage is recycled to the first stage.

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The four 5x5 dot patterns are as follows:

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AUSTRALIA
Patents Act 1990

COMPLETE SPECIFICATION
STANDARD PATENT

Applicant(s):

PASMINCO AUSTRALIA LIMITED
A.C.N. 004 074 962

Invention Title:

PROCESS FOR RECOVERING METAL VALUES

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nickel at mine sites exists but uses solvent extraction/electrowinning (SX/EW). Solvent extraction for zinc is technically much more difficult and can only be used in special circumstances.

5 In addition to these limitations there is a need for a mine site compatible process to recover zinc from low grade feed materials. Flotation is used for recovering zinc sulfide from ore, but this process often is able to
10 recover only 70-80% of the zinc into a form able to be treated at conventional zinc smelters. There is a need to recover the other 20-30% of zinc now lost into the mine tailings dam. It would be uneconomic and impractical to transport such material to a remote dedicated smelter for
15 treatment, and disposal of residues from such a smelter would be prohibitive when treating such a low grade of feed.

The specifications of US Patent Nos. 4676828, 4606763, 4505744, 4440569 as well as the specification of
20 the International Patent Application published under the number WO 94/21830 describe processes for direct leaching of zinc sulfide materials. The specification of US Patent 4676828 describes the Vieille-Montagne direct leach process, which has the following features:

- 25 • Two stage leaching, with the 1st stage under pressure leaching conditions (ie high pressure, and a temperature above the melting point of sulfur) and a 2nd stage at atmospheric pressure, <105°C with oxygen sparging. The 1st stage solution contains
30 20-60 g/L H_2SO_4 , 1-5 g/L Fe^{3+} and is integrated into a conventional electrolytic zinc circuit. The 2nd atmospheric pressure stage produces solution containing 35-160 g/L H_2SO_4 and 2-3 g/L Fe^{3+} which is fed to the 1st stage.
- 35 • Possible extension to a third stage producing solution containing 4-8 g/L H_2SO_4 and 1-2 g/L Fe^{3+} .
- Integration with an existing electrolytic zinc

circuit is required, stand alone operation is not claimed. Maximum treatment of zinc concentrate is claimed to be 75-80% of the total, the rest requiring conventional roasting.

- 5 • Flexible feed requirements are claimed, in respect of the amount of zinc concentrate treated as a proportion of the total, eg from 30-80% the remainder being roasted. Flexible feed grade is not claimed.
- 10 • After leaching, stages of neutralisation using calcine, goethite precipitation, purification using zinc dust, and electrowinning of the zinc are included in the claims.

15 The specifications of US Patent Nos. 4606763, 4440569 and 4505744 as well as that of the International Patent Application published under number WO 94/21830 describe the Sherritt-Cominco process for pressure leaching zinc sulfide containing materials, particularly the two stage pressure leach presently being used by Hudson Bay Mining & Smelting. The process described particularly in the specification of the International Patent Application published under number WO 94/21830 and the specification of US Patent No. 4505744 disclose the following features:

- 25 • Counter-current two stage leaching of zinc sulfide containing material in two pressure leach autoclaves sparged by oxygen. High pressure and temperature are used, ie. above the melting point of sulfur.
- 30 • Treating the product solution with zinc oxide, limestone or related materials, with sparging by oxygen to precipitate iron as goethite and neutralise residual acid.
- 35 • Purifying the solution using zinc dust and electrowinning the zinc.
- Specific mention that the process is suitable for a 'greenfields' or stand alone application.

Both the Vieille-Montagne direct leach process and the Sherritt-Cominco direct leach process fail to meet

range from 3-5. Under these conditions, iron precipitates as goethite. Preferably, the leachate is maintained at a temperature in the range between 55 and 95°C and preferably 70 to 90°C during goethite precipitation.

5 Other impurities such as copper, cobalt, nickel and cadmium may be removed from the leachate by cementation using zinc dust. The zinc dust may be activated with antimony or arsenic compounds. During cementation, the leachate is agitated and the temperature maintained in a
10 range from 70 to 90°C and preferably 80 to 85°C.

In the case of zinc sulphides, zinc may be recovered from purified leachate by conventional electrowinning processes.

15 Preferred embodiments of the invention are described with reference to a flow diagram shown in Figure 1.

The flowsheet consists of 4 sections:

- A counter-current leaching stage operated at atmospheric pressure and $\leq 100^\circ\text{C}$.
- 20 • An iron precipitation stage where goethite (FeOOH) is precipitated using oxygen containing gas sparging and limestone or lime neutralisation.
- A purification stage using zinc dust.
- 25 • Electrowinning of the zinc metal via conventional methods.

The features of each stage are discussed below.

Leaching is carried out in two counter-current stages. Feed solids containing zinc sulfide may be of any grade and composition, but preferably fall into the range
30 10-60% Zn. The solids are added to the first stage of leaching, consisting of one or more agitated tanks. Oxygen containing gas is injected into one or more of the leach tanks, which may operate at a temperature between 75°C and the boiling point but preferably operate at 85-100°C. The
35 first stage of leaching may have a residence time of 0.5-24 hours, preferably 0.5-4 hours. Part of the zinc sulfide is leached in the first stage and the leach solution is

conditioned for feeding to the Goethite Precipitation stage. Partly leached solids are separated for example using a thickener and are sent to the second leach stage. Sufficient solution is also sent to the second leach stage to assure appropriate operating conditions, for example acidity. The leach solution may contain Fe^{3+} 0-30 g/L, Fe^{2+} 5-50 g/L, H_2SO_4 0-30 g/L and Zn 50-160 g/L preferably Fe^{3+} 0-10 g/L, Fe^{2+} 5-30 g/L, H_2SO_4 0-20 g/L and Zn 120-150 g/L.

- The second stage of leaching is fed partially leached solids plus sufficient first stage leach solution to maintain appropriate composition in the second stage leach tanks. Spent electrolyte typically containing H_2SO_4 150-200 g/L, Zn 40-70 g/L and preferably H_2SO_4 160-170 g/L, Zn 50 g/L is added to the tanks, preferably to the first tank. Additional sulfuric acid may also be added to maintain the sulfate balance. The second stage leach consists of one or more agitated tanks, preferably 4 in series, operating at a temperature between 75°C and the boiling point, preferably 85-100°C. The second stage of leaching may have a residence time of 1-36 hours, preferably 1-24 hours. Oxygen containing gas is injected into one or more of the tanks. Extraction of zinc from the solids is completed by the end of the second stage of leaching, preferably with >95% zinc leached. The residual solids are separated from the leach solution, which is fed to the first leaching stage. Second stage leach solution may contain Fe^{3+} 1-50 g/L, Fe^{2+} 5-50 g/L, H_2SO_4 10-50 g/L and Zn 50-160 g/L preferably Fe^{3+} 10-25 g/L, Fe^{2+} 10-25 g/L, H_2SO_4 10-35 g/L and Zn 80-130 g/L. Separation of the residual solids may be effected using a thickener and/or a filter. It may be appropriate to recycle some of the residue solids back into the second stage of leaching to act as a seed. Seeding is a well practised art and is known to improve both precipitation and solids handling properties. Washing of the solids with water may be used to recover entrained zinc. The solids, which contain elemental sulfur, pyrite, lead sulfate, jarosites, and

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silver may be further processed to recover metal values.

Leaching of zinc and other sulfides in the feed material is thought to be effected by ferric sulfate.

Ferric ions are regenerated by reaction of ferrous ions, oxygen and acid. The reactions may be represented as:



Leaching of iron may be minimised by facilitating precipitation of jarosites in the second stage of leaching or by treating feed materials containing iron mostly in the form of pyrite. Hydronium jarosite may be precipitated by maintaining suitable conditions of acidity, Fe^{3+} concentration and temperature. Other jarosites may be precipitated by addition or leaching of appropriate species, for example Na^+ , K^+ , NH_4^+ .

Goethite precipitation was effected by injecting oxygen containing gas into a series of agitated tanks operated at 55-95°C, preferably 60-90°C. Limestone or lime is added to control pH_{25} to 2.5-5.5, preferably 3.0-5.0. Precipitation of goethite may be used to purify the leach solution of iron, arsenic, antimony and other impurities. Separation of the solids from the purified solution may be effected by a thickener and/or a filter. Washing of the filter cake with water can be used to recover entrained zinc. The composition of the product solution may be 100--160 g/L Zn, <100 mg/L Fe, <5 mg/L As, <5 mg/L Sb, preferably 130-150 g/L Zn, <25 mg/L Fe, <1 mg/L As, <1 mg/L Sb.

Solution from the goethite stage was further purified by cementation using zinc dust. The cementation stage may be operated in batch or continuous mode. Zinc dust may be activated with antimony or arsenic compounds. Activated zinc dust was used to remove impurities such as Cu, Co, Ni and Cd. The cementation stage employs agitated

tanks and may be operated over a wide range of conditions, but preferably from 70°C to 90°C, and more preferably 80-85°C. A second stage of zinc dust addition may be included to improve removal of elements such as Co and Cd.

- 5 The composition of the product solution may be 100-160 g/L Zn, <100 mg/L Fe, <2 mg/L Cu, <1 mg/L Co, <1 mg/L Ni, <5 mg/L Cd, preferably 130-150 g/L Zn, <10 mg/L Fe, <0.5 mg/L Cu, <0.8 mg/L Co, <0.5 mg/L Ni, <1 mg/L Cd.

- 10 Purified solution is subjected to electrowinning according to well known art. For example this includes electrowinning from recirculating electrolyte containing 170 g/L H₂SO₄, 55 g/L Zn and 5 g/L Mn. Electrowinning is commonly effected using aluminium cathodes and lead-silver alloy anodes, at a temperature of 37-41°C with a
15 current density of 450-750 Am⁻². Surface active agents which are usually organic compounds, antimony and strontium carbonate may be added to improve zinc deposition and to minimise acid mist generation. Cathode zinc deposits may be stripped at intervals of 16-72 hours by manual or automatic
20 means. The quality of the zinc typically meets High Grade (HG) or Special High Grade (SHG) standard.

The invention differs from prior art in several respects. These include:

- Ability to operate stand-alone at a mine site. No
25 materials are required other than those commonly available to zinc sulfide mine sites, and production of zinc metal of acceptable grade may be achieved without integration with an established smelter.
- Flexibility to treat a wide range of zinc containing
30 materials, for example containing up to 60% Zn, 2-35% Fe, 0-20% Pb. All common impurities may be handled without special consideration.
- Suitability for small scale operations. The prior
35 art processes require use of pressurised leaching vessels such as autoclaves, which are not suited to small scale or short lifetime applications.
- An ability to integrate zinc metal production better

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with mine operations to increase overall zinc recovery from ore to metal.

- No production of hazardous or harmful gases, such as SO_2 , and all residues and wastes may be integrated with existing mine site residues. For example by siting metal production at the mine, leach residues may be blended with mine tailings or returned underground.
- The process of the present invention does not require high temperature or pressure and does not require special procedures to cope with molten elemental sulfur.

Examples that further illustrate preferred embodiments of the invention follow.

Example 1 Two stage counter current batch leaching of conventional zinc concentrate

1.5 litres of solution containing 16 g/L Fe^{3+} , 10 g/L Fe^{2+} , 22 g/L H_2SO_4 and 139 g/L Zn was heated in a baffled reactor to 95°C and 100 g of dried zinc concentrate containing Zn 47%, Fe 10%, Pb 2% added with agitation using a Rushton type turbine at 800 s^{-1} . Oxygen gas was injected under the agitator at 100 mL/min. Agitation was maintained for 2 hours, after which time the gas sparging was turned off, flocculant added and the slurry allowed to settle in the reactor. A small pump was used to withdraw 420 mL of supernatant solution, which was replaced by 420 mL of spent electrolyte containing 172 g/L H_2SO_4 and 50 g/L Zn, and an additional 20 mL of 98% sulfuric acid. Agitation and oxygen sparging is restarted and continued for 21 hours at 95°C. The slurry is filtered and the residue washed with excess water. Analysis of the dried leach residue showed it to contain 0.9% Zn, 8% Fe, 4% Pb. The 420 mL of solution withdrawn after 2 hours contained 2 g/L Fe^{3+} , 36 g/L Fe^{2+} , 16 g/L H_2SO_4 and 160 g/L Zn. The final solution contained 13 g/L Fe^{3+} , 8 g/L Fe^{2+} , 55 g/L H_2SO_4 , and 158 g/L Zn. Zinc extraction from feed was calculated to be 99%.

at 66 mL/min as a 720 g/L slurry in zinc sulfate solution. Spent electrolyte containing 170 g/L H_2SO_4 and 50 g/L Zn was fortified to 254 g/L H_2SO_4 using 98% sulfuric acid and was pumped into the initial second stage tank at 108 mL/min. Oxygen gas was sparged below the agitator of each tank, which was held at 95°C. Underflow from the first stage thickener was pumped to the initial tank of the second stage at 280 mL/min. Water at 85 mL/min was pumped to Tanks 2 and 4 to make up for evaporation. Second stage thickener underflow was pumped out at 110 mL/min. 5 mL/min of flocculant solution was pumped to each thickener.

After 3 days of operation the pilot plant reached steady state. After 4 days the dry washed leach residue was found to contain 0.5% Zn, 27% Fe, 6% Pb, which corresponds to a zinc extraction of 99%. The composition of first stage thickener overflow was 7 g/L Fe^{3+} , 25 g/L Fe^{2+} , 12 g/L H_2SO_4 , 153 g/L Zn. The composition of second stage thickener overflow entering the first stage leach tank was 24 g/L Fe^{3+} , 8 g/L Fe^{2+} , 27 g/L H_2SO_4 , 131 g/L Zn.

Example 4: Continuous goethite precipitation using limestone

A continuous pilot plant assembly consisting of 1 x 50 L and 3 x 12 L agitated tanks was assembled in a cascade such that the tanks could overflow from one to the next. Solution obtained from the leach pilot plant described in Example 3 was pumped into the first tank at 100 mL/min. Limestone slurried in zinc sulfate solution was pumped to the first and second tanks under computer control to pH 4 and 4.7 respectively, measured at 25°C (pH_{25}). Water was pumped to the first tank at 25 mL/min to make up for evaporation. Air was sparged into each tank below the agitators, which were of the Rushton design and operated at 400-500 s^{-1} . Temperature was maintained at 90°C in each tank. Produced goethite slurry was collected in a storage tank. Total residence time was approximately 9 hours. The goethite precipitation pilot plant was operated

continuously for 30 hours, and reached steady state after 24 hours. At that time the pH in the 4 tanks was 3.7, 4.7, 4.1 and 4.0 respectively. Composition of the feed solution was 146 g/L Zn, 29 g/L Fe, 0.5 g/L Cu. Composition of the product solution was 144 g/L Zn, 0.05 g/L Fe, 0.2 g/L Cu.

Example 5: Batch zinc dust purification

A 1.5 L batch of solution obtained by filtering goethite slurry produced during operation of the pilot plant described in Example 4 was heated to 85°C in a 3 L baffled vessel. Nitrogen gas was bubbled into the solution at 30-50 mL/min to displace atmospheric oxygen. Upon reaching temperature 24 mg of potassium antimony tartrate was added followed shortly by 7.5 g of coarse zinc dust. Agitation was continued for 30 minutes then the slurry filtered using a vacuum filter. Composition of the feed solution was 170 mg/L Cu, 240 mg/L Cd, 17 mg/L Co, 3 mg/L Ni, 15 mg/L Fe. Composition of the purified solution was <0.1 mg/L Cu, 0.1 mg/L Cd, <0.1 mg/L Co, 0.6 mg/L Ni, 7 mg/L Fe.

Example 6: Electrowinning

A batch of 3.5 L of purified solution doped with surface active agents, potassium antimony tartrate and strontium carbonate, was continuously pumped at 1.0 mL/min into a small electrolytic cell containing 650 mL of spent electrolyte of composition 170 g/L H₂SO₄ and 50 g/L Zn. The cell contained a 5.5 x 12 cm aluminium cathode and 2 similarly sized 0.6%Ag/Pb anodes. Solution overflowing the cell from an exit spigot was collected in a storage vessel. A direct current of 6.5 A was applied to the cell. Temperature was maintained at 37°C. Composition of the feed solution was 153 g/L Zn, 10 mg/L Fe, <0.1 mg/L Cu, <0.1 mg/L Cd, 1.5 mg/L Co, 0.1 mg/L Ni, 11.6 g/L Mn. After operation for 43 hours the cathode was removed from the cell and the zinc deposit water washed and manually stripped. The weight of the cathode was 270 g,

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corresponding to a current efficiency of 79%. The composition of the cathode deposit was 6 ppm Fe, 2 ppm Cu, 1 ppm Cd, 1 ppm Co, <1 ppm Ni, 30 ppm Pb.

5 **Example 7: Integrated continuous pilot plant leaching of low grade zinc concentrate**

The counter-current leach pilot plant described in Example 3 was augmented by a goethite precipitation stage consisting of 1 x 50 L and 4 x 12 L agitated tanks, a
10 cementation stage consisting of a single 150 L capacity conical bottomed batch agitated tank and an electrolytic cell equipped with one industrial size aluminium cathode of 90 x 55 cm and two 0.6% Ag/Pb anodes of similar size. The cell was cooled using recirculated cooling water and a
15 water jacket. The fully integrated pilot plant was operated continuously for 21 days. Conditions are summarised below:

Leaching: two stage counter current at 95°C, oxygen sparging to all tanks, spent electrolyte at 100 mL/min to
20 Tank 1 fortified from 170 to 210 g/L H₂SO₄, feed solids at 19-24% Zn, 24-30% Fe and 2-3% Pb pumped to the first leach stage at 58-72 mL/min as an 800 g/L slurry in recycled leach solution. Approximate residence times for the first and second leaching stages were 3 and 19 hours
25 respectively. Leach residue was accumulated and filtered and washed using a recessed plate filter press, with filtrate and wash water returned to the leach.

Goethite precipitation: 5 tanks in series at 85°C, oxygen
30 sparging to all tanks, limestone slurried in recycled goethite solution and pumped to Tank 1 and 2 under computer control respectively to pH₂₅ 4.0 and 4.8. Goethite slurry was accumulated and filtered and washed using a recessed plate filter press. Wash water was returned to the leach or
35 goethite precipitation stage.

Cementation: 1 batch tank operated once per day. The batch

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tank was charged with goethite solution and heated to 80°C. The batch vessel was equipped with a nitrogen gas bubbler to displace dissolved oxygen from the solution. With agitation 16 mg/L of potassium antimony tartrate was added followed by 5 g/L of coarse zinc dust. After 30 minutes the slurry was filtered through a small plate and frame filter press. The filtrate was analysed to determine whether quality was acceptable for electrowinning, and if so was pumped to the cell feed stock tank. If quality was not acceptable the solution was subjected to a repeat of the batch cementation.

Electrowinning: Solution doped with surface active agents and antimony as potassium antimony tartrate, and was fed continuously into the cell at 100 mL/min. Strontium carbonate was pumped into the cell as a slurry in water. Current was controlled to maintain spent electrolyte acidity at 170 g/L, and was usually in the range 450-500 A. Cell voltage was 3.2V and temperature maintained at 37-39°C. The single cathode was removed after each 48 hours, stripped of zinc, water washed and scrubbed and returned to the cell. Current efficiency was typically 91-94%. Spent electrolyte exiting the cell via an overflow spigot was accumulated in a storage tank before being fortified with acid and pumped to the second leach stage.

Composition of various streams are given in Table 1.

TABLE 1

Stream or material	Flowrate mL/min	Composition g/L or %						
		Fe ³⁺	Fe ²⁺	H ₂ SO ₄	Zn	Cu	Cd	Co
Portified spent electrolyte	100	-	-	210	50	-	-	-
Second stage leach sol'n	380	23	9	20	130	1.0	0.2	0.03
First stage leach sol'n	110	5	22	7	155	1.1	0.2	0.03
Gothite product sol'n	105	-	0.02	-	150	0.2	0.2	0.03
Concentration product sol'n	100	-	0.008	-	145	0.0005	0.0005	0.0005
Spent electrolyte	95	-	-	170	50	-	-	-
	g/min	Zn	Fe	Pb	Cu			
Feed solids week 1-2	54	19	30	3	0.2			
Feed solids week 3	44	24	28	2	0.2			
Leach residue week 1-2	-32	1	31	3	0.2			
Leach residue week 3	-32	1	29	3	0.2			
Gothite residue	-30	2	15	-	19			
Zinc cathode	10	>99.99	0.0005	0.0020	-			

Although this invention is primarily for mine site use it is also suitable for installation at a standard zinc hydrometallurgical smelter, either as an expansion to an existing smelter or as a replacement for some of the existing operations.

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8. A process according to any one of claims 1 to 7 wherein the metal sulphide is zinc sulphide and the first

Fe^{3+}	0 - 30 g/L
Fe^{2+}	5 - 50 g/L
H_2SO_4	0 - 30 g/L
Zn^{2+}	50 - 160 g/L

Fe^{3+}	0 - 10 g/L
Fe^{2+}	5 - 30 g/L
H_2SO_4	0 -20 g/L
Zn^{2+}	120 - 150

10. A process according to any one of claims 1 to 9 wherein the process includes a first leachate treatment step of injecting an oxygen containing gas into the first leachate at elevated temperature at a pH₂₅ in a range from 2.5 to 5.5 to precipitate impurities such as iron, arsenic and antimony and separating a third leachate from the precipitate.

12. A process according to claim 11 wherein the temperature lies in a range from 60°C to 90°C.

13. A process according to any one of claims 10 to 12 wherein the pH₂ is maintained in a range from 3 to 5.

15. A process according to any one of claims 10 to 14 wherein the metal sulphide is zinc sulphide and the process includes taking the third leachate and subjecting it to a second treatment step of adding zinc dust to the third leachate to remove other impurities by cementation to

produce a purified leachate and electrowinning zinc from the purified leachate.

16. A process according to claim 15 wherein the zinc dust is activated with antimony or arsenic compounds.

5 17. A process according to claim 15 or claim 16 wherein the second treatment step is performed at a temperature in a range from 60°C to 90°C.

18. A process according to claim 17 wherein the temperature lies in a range from 80°C to 85°C.

10 19. A process for recovering zinc values from an ore or concentrate substantially as hereinbefore described with reference to any one of the examples.

20. A process for recovering zinc values from an ore or concentrate substantially as hereinbefore described with

15 reference to the drawings.



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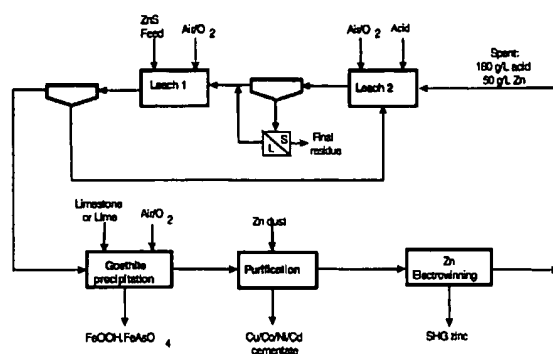


FIGURE 1

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